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Dynamic interfacial tension of some sulphonate systems

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ABSTRACT

Nine pure sodium phenylalkane sulphonates, namely, 3-phenyltetradecane, 5-pheyltetradecane, 7-phenyltetrdecane, 3-phenylhexadecane, 5-phenylhexadecane, 7-phenylhexadecane, 1-phenyldode-cane, 1-phenyltetrdecane and 1-phenylhexadecane sodium sulphonates, were prepared and their capabilities for lowering dynamic interfacial tension (D-IFT), were evaluated in n-octane/NaOH aqueous systems. The effects of surfactant structure and the concentration of added NaOH on the tension behaviour of these anionic surfactant systems, were studied. Tension behaviour of surfactant are considered the backbone for evaluating and designing practical formulations used for surfactant flooding systems.

Keywords: Sulphonate-alkane-NaOH system. Sulphonate structure and tension behaviour Dynamic interfacial tension and Alkalinity.

INTRODUCTION

During the past decades, more and more attention has been drawn to the enhanced oil Recovery (EOR) projects and, in particular, surfactant flooding which is considered to be one of the most promising exploitation modes. A considerable amount of reaearch work concerning the screening of formulations and mechanisms of surfactant flooding have been carried out by petroleum chemists [Shah, D.O. *et al.,* (1972), Gale, W.W. and Sandvik, E.I. (1973), Wilchester, H.I. (1974)]. The Surfactants used in their early work were mainly petroleum sulphonates which consist of complex components of uncertain structures [Sandvik, E.L. *et al.,* (1976), Knaggs, E. (1976), Smith, G.D. (1979)]. When such a kind of surfactant was used for flooding systems, several technical problems appeared. Interfacial tension, (IFT) measurements between these surfactant aqueous systems and crude oil, have not given explicable results. The great advantage of replacing crude oils by alkanes, in low tension studies, allows use of a whole scale of oil phase properties (form n-pentane to n-heptadecane) [Wade, W.H. and Schechter, R.S. (1977), Shah, D.O. and Walker, R.D. (1978), Wade, W.H. *et al.,* (1978), Schechter, R.S. and Wade, W.H. (1980/1981)]. Moreover, this scale can also be used for comparison and evaluation of different surfactant systems and the introduction of the equivalent alkane carbon number (EACN) concept [Sandvik, E.L. *et. al.,* (1976), Knaggs, E. (1976), Smith, G.D. (1979)].

In short, using surfactants of definite structure and adopting the alkane scale are necessary for achieving explicit explanation for the interfacial behaviour studies of surfactant systems used for EOR [Wade, W.H. and Schechter R.S. (1977), Shah, D.O. and Walker, R.D. (1978), Wade, W.H. *et al.,* (1978)]. Many other variables, such as surfactant molecular weight and concentration, cosurfactant type and concentration, electrolyte and alkali, have been investigated easily in current research works [Barakat. Y. *et al.,* (1983), Rudin. J., and Wasan. D.T. (1992), Zhang. S.B. *et al.,* (2004), Feng. J. *et al.,* (2004), Rosen, M.J. *et al.,* (2005)].

In this study, five pure terminal-and mid-position phenylalkane sulfonate sodium salts, were

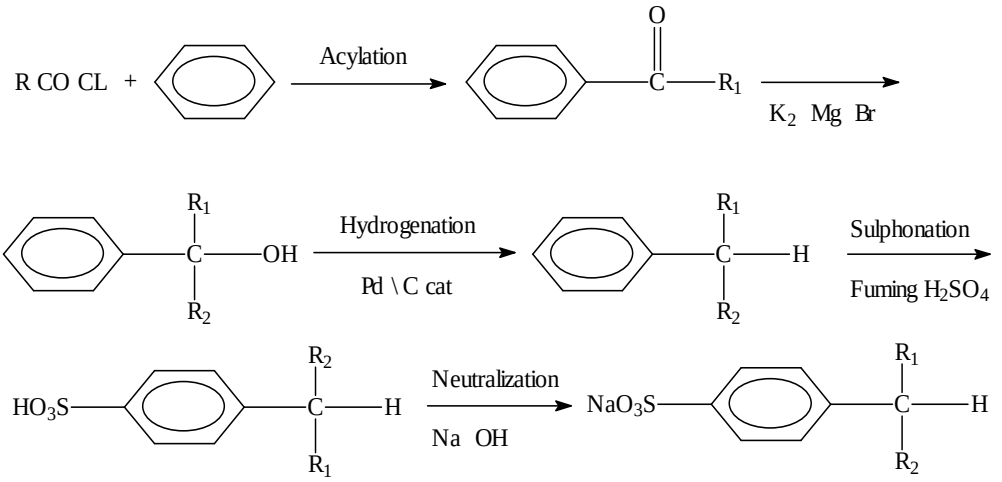
prepared and the interfacial tension behaviour of these sulfonates against oil phase alkane carbon number (ACN). Also, the effect of added n-pentanol and n-octanol on the IFTs of these phenylalkane sulphonates, were studied.

EXPERIMENTAL

Surfactants

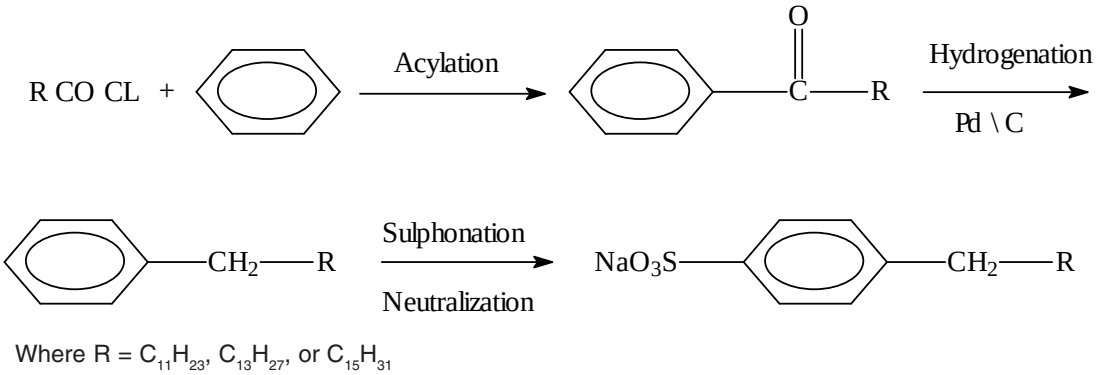
Nine sodium phenylalkane sulphonates of definite structure and high purity were prepared following the synthesis scheme which has been reported in literature [Doe, P.H. *et al.,* (1977), El-Mergawy. S.A. (1989)].

1. Preparation of 3.phenyltetradecane, 5-phenyltetradecane, 7-phenyltetradecane, 3-phenylhexadecane, 5-phenylhexadecane and 7-phenylhexadecane, was conducted in the steps shown in figure [1(a)].
2. Preparation of 1-phenyldodecane, 1-phenyltetradecane and 1-phenylhexadecane, was conducted in the steps shown in figure [1(b)].



Where R_1 = $C_{11}H_{23}$, C_9H_{19}, C_7H_{15}, and
R_2 = C_2H_5, C_4H_9, C_6H_{13}, respectively
(For $3FC_{14}$ S, $5FC_{14}$ S and $7FC_{14}$ S).
and R_1 = $C_{13}H_{27}$, $C_{11}H_{23}$, C_9H_{19}, and
R_2 = C_2H_5, C_4H_9, C_6H_{13}, respectively
(For $3FC_{16}$ S, $5FC_{16}$ S and $7FC_{16}$ S).

Fig. 1: (a) Synthesis scheme for the mid-position phenylalkane sodium sulphonates



Where R = $C_{11}H_{23}$, $C_{13}H_{27}$, or $C_{15}H_{31}$

Fig. 1: (b) Synthesis scheme for the terminal-position phenylalkane sodium sulphonates

After being purified through desalting and deoiling steps [El-Mergawy. S.A. (1989)], the prepared surfactants were identified by MS, IR and HLB which indicated a purity not less than 95%.

CMC and γ_{CMC} Determination

Surface tension of the prepared sulphonates were measured as a function of surfactant concentration at 28°C for the mid-position phenylalkane sodium sulphonates and at 60°C for the terminal-position ones using Dagnon-Abribat Tensiometer, Prolabo [El-Koly, S.A. (1993)]. The critical micelle concentration (cmc) values were obtained by plotting the measured surface tension versus the logarithm of surfactant concentration (or concentration on a log scale), At the intersection of the straight line portions of the graph, the cmc can be located through the least-squares regression analysis [Draper. N.R and Smith, H. (1968)] as has been reported [Barakat, Y. *et al.,* (1989), Rosen, M.J. Chapter 3. (1989)]. Figure (2) is an illustration for the location of cmc and γ_{cmc} values the obtained

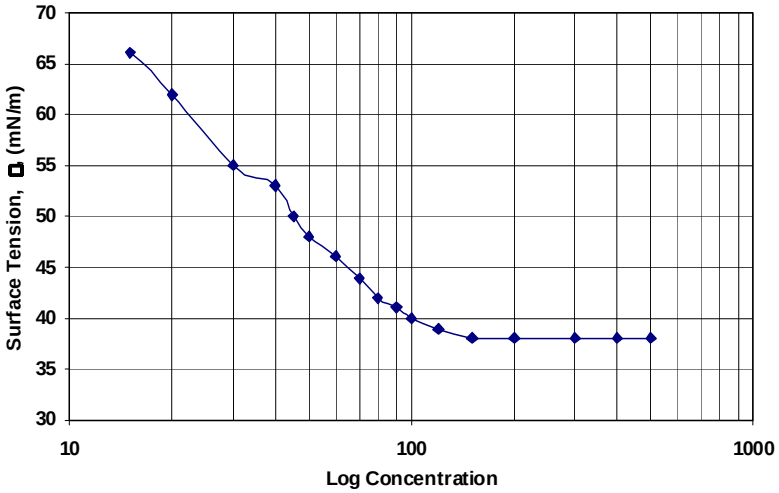
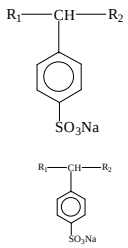


Fig. 2: An illustrative figure for the determination of CMC and γ_{cmc} values of a surfactant.

Table 1: CMC and γ_{cmc} values of the prepared mid-and terminal-position phenylalkane sodium sulphonates

Surfactant structure	R1	R2	Surfactant designation	CMC (mmole /L)	Cmc (mN/m)	Temp. (°C)
	C_2H_5	$C_{11}H_{23}$	3F C_{14}5	190	34.1	28
	C_4H_9	C_9H_{19}	5F C_{14}5	250	32.3	28
	C_6H_{13}	C_7H_{15}	7F C_{14}5	340	30.6	28
	C_2H_5	$C_{13}H_{27}$	3F C_{16}5	85	32.5	28
	C_4H_9	$C_{11}H_{23}$	5F C_{16}5	175	30.1	28
	C_6H_{13}	C_9H_{19}	7F C_{16}5	260	27.2	28
		1Φ C_{12}	5*	310	35.3	60
		1Φ C_{12}	5*	150	36.7	60
n= 11,13,15		1Φ C_{12}	5*	55	36.8	60

*These surfactants have Krafft points,33, 47, and 58°C, [(El-Mergawy. S.A. (1989), Rosen, M.J. (1989)]

cmc and γ_{cmc} values are given in Table (1).

Dynamic Interfacial Tension (D-IFT)

D-IFT between sulphanate aqueous systems and n- Octane, was measured at 28°C using the spinning interfacial tensiometer developed by Cayias, Schechter and wade [Cayias, J.L. *et al.,* (1975)] the spinning tube was filled first with the aqueous surfactant solution then a droplet of an oil phase (n- octane), was introduced through a special syring . Temperature control was achieved using the built – in cell heater and insulating muff provided on Model 300 Spining Drop tensiometer, manufactured by the University of Texas at Austin , USA. For the work reported herein, the D-IFT Values of 1- phenylalkane sulphantes , were measured at 60°C to avoid precipitation of surfactants.

RESULTS AND DISCUSSION

The Prepared Sulphonates

Two sets of phenyltetradecane and phenylhexadecanes sodium sulphonate isomers, were prepared following the synthesis route shown in Figure (1(a)). Each set consists of three isomers in which the benzene ring is attached to carbon atoms number 3,5 and 7. Thus , the prepared sulphantes are designated $3\Phi C_{14}S$, $5\Phi C_{14}S$, $7\Phi C_{14}S$ in the first set and $3\Phi C_{16}S$, $5\Phi C_{16}S$, $7\Phi C_{16}S$ in the second set. In Figure 1(b), 1-phenyldodecane, 1-phenyltetradecane and 1-phenylhexadecane were also prepared and designated $1\Phi C_{12}S$, $1\Phi C_{14}S$ and $1\Phi C_{16}S$, respectively.

Surface Tension of Some Phenylalkane Sulphonates

g_{cmc} values of $3\Phi C_{14}S$, $5\Phi C_{14}S$ and $7\Phi C_{14}S$ in pure water at 28°C were measured from the surface tension-concentration isotherm as illustrated in Figure (2). Similarly, g_{cmc} values of the three other isomers: $3\Phi C_{16}S$, $5\Phi C_{16}S$ and $7\Phi C_{16}S$, were measured. The obtained γ_{cmc} values are listed in Table (1) alongwith the corresponding cmc expressed as micromoles per litre (μ mole/L.).

Data in table (1) reveals that moving the point of attachment of benzene towards the more central carbon atoms along the linear alkyl chain resulted in an increase in the cmc and, on the contrary, a lowering in g_{cmc} value of these isomers. γ_{cmc} values of $3\Phi C_{14}S$, $5\Phi C_{14}S$ and $7\Phi C_{14}S$ were 34.1, 32.3 and 30.6 mN/m, respectively. Similarly, γ_{cmc} of $3\Phi C_{16}S$, $5\Phi C_{16}S$ and $7\Phi C_{16}S$ were 32.5, 30.1 and 27.2 mN/m, respectively. It is well-known that the smaller γ_{cmc} is, the more capability for lowering the surface tension. So the capabilities for lowering the interfacial tension of the tetradecylbenzene sulphonate isomers are in the order: $7\Phi C_{14}S > 5\Phi C_{14}S > 3\Phi C_{14}S$, and that of hexadecylbenzene sulphonate isomers are in the same order, i.e., $7\Phi C_{16}S > 5\Phi C_{16}S > 3\Phi C_{16}S$. It is known also that the surface energy of methyl group (CH_3) is smaller than that of methylene group (CH_2). The alkyl chain of each of these isomer has two CH_3 groups. The surfactant provides more capability for lowering surface tension if the two CH_3 groups are present on the uppermost layer. Different

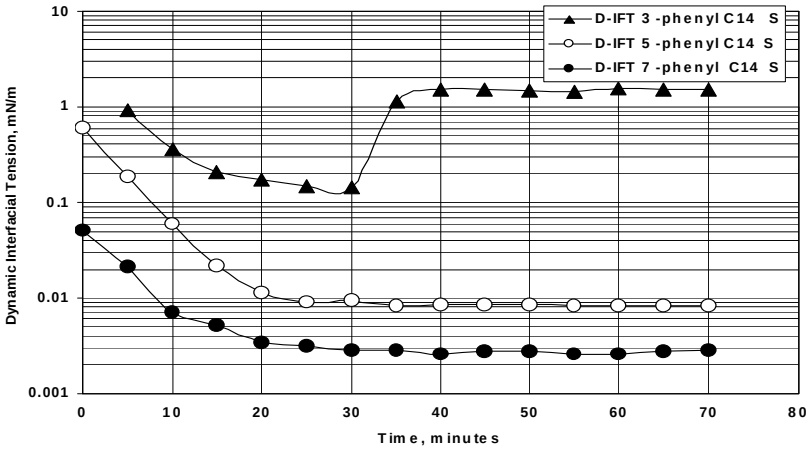


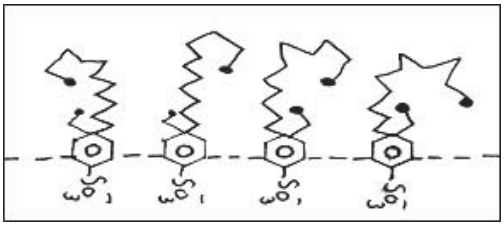
Fig. 3: Dynamic interfacial tension behaviour of three phenyltetradecane sodium sulphonate isomers

surface activities of three isomers could be demonstrated by adopting an imaginary surface molecular arrangement model [Zhang. S.B, *et al.,* (2004)]. Shown in figure (3).

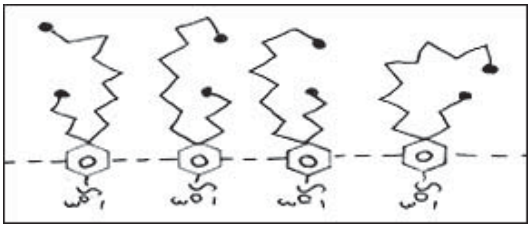
It is well known that molecules with the same electric charge repel each other. Having the same hydrophilic group (SO_3^-), a certain distance is assumed between the surfactant molecules. This distance is equal for the three tetradecylbenzene sulphonate isomers. $3\Phi C_{14}S$ isomer has a long linear lipophilic group ($R_2 = C_{11}H_{23}$, Table 1) and is more spatial around molecules that would allow the single bond of carbon chain turn around freely, so that this longer chain winds itself exposing CH_2 group on the outermost layer and to have the shorter R_1 chain covered (Figure 4a), so the surface energy of $3\Phi C_{14}S$ is the highest. The difference in length between R_1 and R_2 of $5\Phi C_{14}S$ is smaller.

The longer R_2 chain is not easy to wind itself and the shorter R_1 chain remained uncovered by R_2, so comparatively more CH_3 groups are on the outermost layer (Figure 4b) and the surface energy of $5\ \Phi\ C_{14}$ S, is lower than $3\ \Phi\ C_{14}S$. The two chains, R_1 and R_2 of $7\ \Phi\ C_{14}S$ are both short and similar in length. The posiibility of winding themselves or covering each other is rare. The two terminal CH_3 groups of each molecule are exposed on the outermost layer (Figure 4C), So the surface energy of $7\Phi\ C_{14}S$ is the lowest. It can be inferred that the surface activity of $3\ \Phi\ C_{16}\ S > 5\ \Phi\ C_{16}\ S > 7\ \Phi\ C_{16}$ S. Based on these result, one can reach a conclusion that molecular structure of surfactant would dictate the molecular arrangement state and the fraction of coverage of the CH_3 group decide the capability of lowering the surface tension.

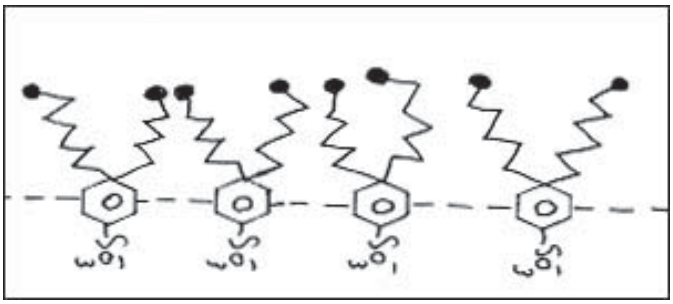
Terminal-position phenylalkane sodium sulphonates, $1\ \Phi\ C_{12}$ S, $1\ \Phi\ C_{14}$ S and $1\ \Phi\ C_{16}$ S have krafft points 38, 47 and 59°C, respectively [El-Mergawy. S.A. (1989)]. For the maximum effectiveness in surface tension reduction, surfactants are normally used above their krafft point [El-Mergawy. S.A. (1989), Rosen, M.J. Chapter 5, (1989)]. That is why cmc and g_{cmc} values of these surfactants, are measured at 60°C, Table (1) lists the obtained values. Increasing the length of the



(a) $3\Phi C_{14}$ S Interface CH_3



(b) $5\Phi C_{14}$ S Interface CH_3



(c) $7\Phi C_{14}$ S Interface CH_3

Fig. 4: An Imaginary molecular arrangement illustrating that: (a) No CH_3 groups are exposed (b) CH_3 groups of the longer chains are exposed, and (c) CH_3 groups of two chains are exposed on the outermost layer.

linear alkyl group from C_{12} to C_{16} resulted in a considerable decrease in cmc values, whereas an insignificant change in γ_{cmc} values, was detected.

Dynamic Interfacial Tension in Alkane/Aqueous System

In figure 3, similar tendency is shown by three curves. At the begining, the interfacial tension decreases as time goes on, then reaches the minimum; that is, the equilibrium is reached. At the beginning, the adsorption rate, at n-octane/ water interface, is faster than the desorption rate, resulting in the decrease of interfacial tension [Rosen, M.J. Chapter 2. (1989)]. As both rates become equal, the interfacial tension would not vary any more and equilibrium is established.

The minimum interfacial tension of 3 Φ C_{14} S, 5 Φ C_{14} S and 7 Φ C_{14} S isomers differ in magnitute.The interfacial tension can be lowered to $1.5x10^{-1}$ mN/m by 3 F C_{14} S, to $8.5x10^{-3}$ mN/m by 5 ΦC_{14} S and to $2.8x10^{-3}$ mN/m by 7ΦC_{14} S, respectively (Figure 3). The minimum interfacial tension of 3 Φ C_{16} S, 5 Φ C_{16} S and 7 Φ C_{16} S isomers is reduced to $9.5x10^{-2}$ mN/m by 3 F C_{16} S, to $4.5x10^{-3}$ by 5 Φ C_{16} S, and to $1.5x10^{-3}$ by 7 F C_{16} S, respectively (Figure 5). This is in accordance with g_{cmc} values given in Table (1).

This reduction in interfacial tension values of three isomers of tetradecyl-and heaxdecyl-benzene sodium sulphonates, can also be explained on molecular structure. As the benzene ring shifts toward the middle of the alkyl chain, the fraction of coverage of CH_3 groups of the surfactant molecules would increase, resulting in the increase of the capability for lowering interfacial tension. It is obvious from figure (6) and (7) that in the investigated sets of tetradecyl- and hexadecyl-benzene sodium sulphonates, the position of phenyl group along the linear alkyl chain is very important.

Dynamic interfacial tension, D-IFT, values decrease when phenyl group approaches the terminal carbon atoms of alkyl chain. D-IFT values of 3 Φ C_{14} S, 5 Φ C_{14} S and 7 Φ C_{14} S can be lowered to $15x10^{-2}$, $85x10^{-3}$ and $28x10^{-4}$ mN/m, respectively. Similarly. D-IFT values of 3 Φ C_{14} S, 5 ΦC_{14} S and 7 Φ C_{14} S can be lowered to $95x10^{-3}$, $45x10^{-4}$ and $15x10^{-4}$ mN/m, respectively. From this sequence, one can deduce that 1-phenyltetradecane and 1-phenylhexadecane sodium sulphonate isomers will have higher D-IFT values than that obtained by 3 Φ C_{14} S or 3 Φ C_{16} S, respectively.

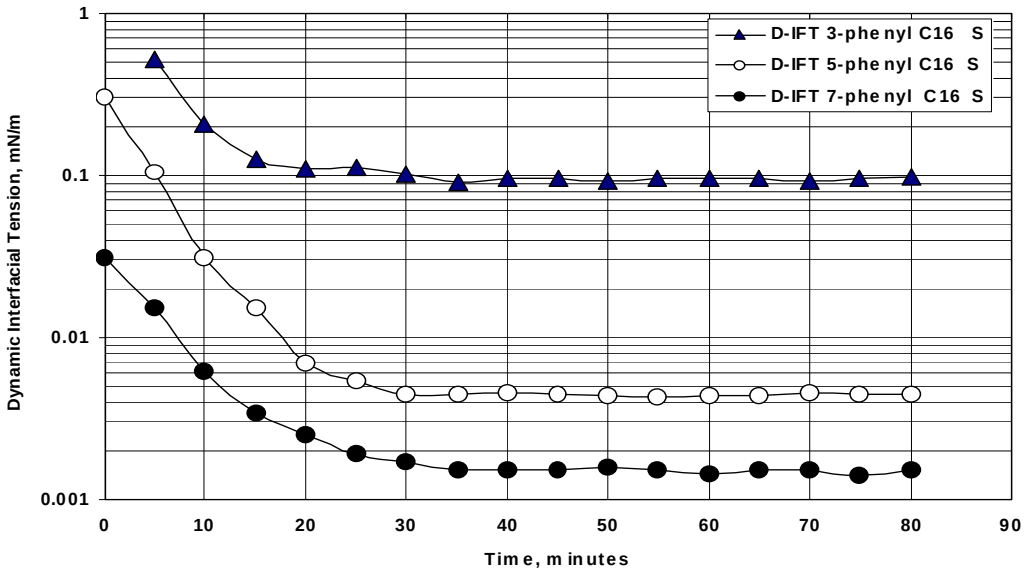


Fig. 5: Dynamic Interfacial tension behaviour of three phenylhexadecane sodium sulphonate isomers

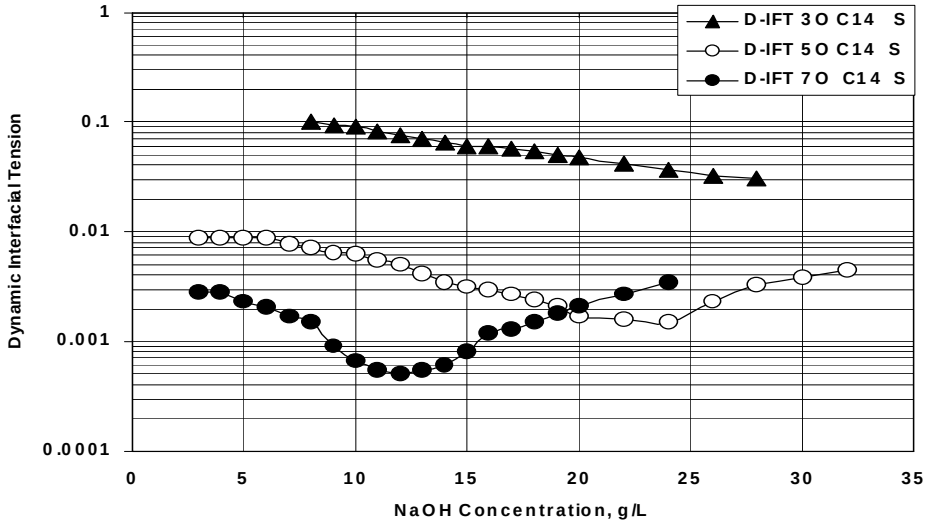


Fig. 6: Dynamic Interfacial Tension of three phenylhexadecane sodium sulphonate isomers against n-Octane as a function of alkalinity

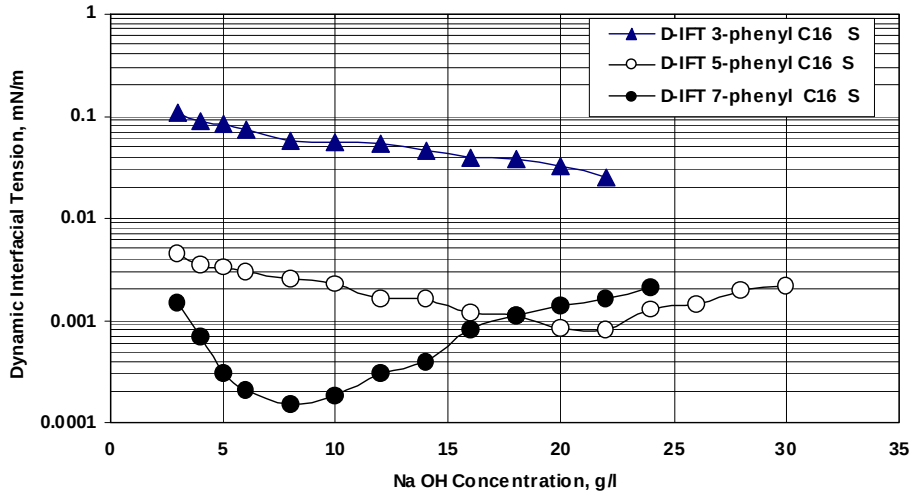


Fig. 7: Dynamic Interfactial Tension of three phenylhexadecane sodium sulphonate isomers against n-Octane as a function of alkalinity.

Effect of Alkalinity on D-IFT

Figures (6) and (7) show that only the dynamic interfacial tension of 3 F C_{14} S and 3 F C_{16} S decrease as alkalinity increases without the appearance of v-shaped curve. However, 3 Φ C_{14} S and 3 F C_{16} S precipitate when alkalinity is greater than 24 and 22g/L, respectively. But each of 5ΦC_{14} S and 7FC_{14} S gave $(D\text{-}IFT)_{min}$ values at their respective optimum alkalinities of 24 g/l and 12g/L NaOH, respectively. Similarly, each of 5ΦC_{16} S and 7ΦC_{16} S gave their $(D\text{-}IFT)_{min}$ values through v-shaped curves at optimum alkalinity of 22 and 8 g/L NaOH. The difference in alkalinity tolerance is attributed to molecular structure, i.e, terminal-

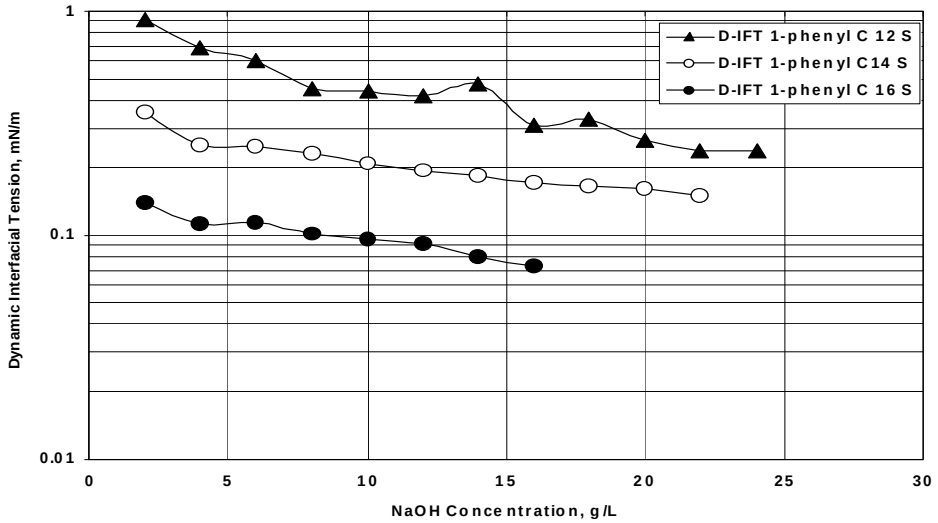


Fig. 8: Dynamic Interfacial Tension of three 1-phenylalkane sodium sulphonates against n-Octane as a function of alkalinity

position phenylalkane sodium sulphonates have the least alkalinity tolerance, whereas, mid-position phenylalkane sodium sulphonates show the highest alkalinity tolerance to NaOH. Some investigators postulated an imaginary surfactant molecular arrangement model illusrating the effects of electrolyte on the interfacial tension of 3-phenyl-, 5-phenyl-, and 7-phenylalkane isomers [Zhao, G.X. (1991)]. The addition of electrolyte to solutions of ionic surfactants in aqueous solution casues an increase in the aggregation number presumably because of compression of the electrical double layer surrounding the ionic heads [Rosen, M.J. Chapter 3. (1989)]. For the investigated anionic phenylalkane sodium sulphonate isomers; Na^+ would compress the double layer and shorten the molecular distance on interface [Zhao, G.X. (1991)]. As NaOH concentration increases, the molecular distance is shortened readily and the number of molecules on the unit area would also increase gradually, then the winding of long chain would tend to be "stretched" gradually, leading to the decrease of interfacial tension.

In figure (8), increasing NaOH concentration casues a steady decrease in D-IFT of 1-phenylalkane sodium sulphonates. However, precipitation of these surfactants was observed at 24, 22, and 16g/l NaOH for $1\Phi C_{12}$ S, $1\Phi C_{14}$ S and $1\Phi C_{16}$ S, respectively. Although D-IFT measurements were carried out at 60°C, i.e., above the krafft point of these surfactants [El-Mergawy. S.A. (1989)]. addition of a co-surfactant is necessary in these formulations in order to prevent precipitation and to achieve lower interfacial tensions [Zhang. S.B. *et al.,,* (2004)].

Conclusions

1. In an alkane/ aqueous system of mid-position phenyl-tetradecane and phenylhexadecane sodium sulphonate isomers, IFT decreases as the phenyl group shifts toward the middle of the alkyl chain.
2. The minimum IFT of the investigated isomers differs in magnitude and their capabilities for lowering IFT follow the sequence: 7-phenyl-isomers > 5-phenyl-isomers > 3-phenyl-isomers. This sequence is in accordance with g_{cmc} values of these isomers.
3. Dynamic interfacial tension minimum $(D\text{-}IFT)_{min}$ values of 5-phenyl-and 7-phenylalkane isomers, are achieved through v-shaped curves at their respective optimum alkalinity. D-IFT of 3-phenylalkane isomers decreases as alkalinity increases without the appearance of v-shaped curve.

4. Ultralow $(D\text{-}IFT)_{min}$ values are obtained by $7FC_{16}$ S and $5FC_{16}$ S isomers if compared with $7FC_{14}$ S and $5FC_{14}$ S. These $(D\text{-}IFT)_{min}$ values are achieved at lower NaOH concentrations.

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